

CHAPTER 7

HYDROTHERMAL ORGANIC SYNTHESIS EXPERIMENTS

EVERETT L. SHOCK

Department of Earth and Planetary Sciences, and McDonnell Center for the Space Sciences,

Washington University, St. Louis, MO 63130, U.S.A.

1. Introduction

The serious scientific debate about spontaneous generation which raged for centuries reached a climax in the nineteenth century with the work of Spallanzani, Schwann, Tyndall, and Pasteur. These investigators demonstrated that spontaneous generation from dead organic matter does not occur (see reviews by Conant, 1953 and Kenyon and Steinman, 1969). Although no aspects of these experiments addressed the issue of whether organic compounds could be synthesized abiotically, the impact of the experiments was great enough to cause many investigators to assume that life and its organic compounds were somehow fundamentally different than inorganic compounds.

Meanwhile, other nineteenth-century investigators were showing that organic compounds could indeed be synthesized from inorganic compounds. In 1828 Friedrich Wöhler synthesized urea in an attempt to form ammonium cyanate by heating a solution containing ammonia and cyanic acid (Wöhler, 1828). This experiment is generally recognized to be the first to bridge the artificial gap between organic and inorganic chemistry, but it also showed the usefulness of heat in organic synthesis. Not only does an increase in temperature enhance the rate of urea synthesis, but Walker and Hambly (1895) showed that equilibrium between urea and ammonium cyanate was attainable and reversible at 100°C. Wöhler's synthesis of urea, and subsequent syntheses of organic compounds from inorganic compounds over the next several decades dealt serious blows to the "vital force" concept which held that: 1) organic compounds owe their formation to the action of a special force in living organisms, and 2) forces which determine the behavior of inorganic compounds play no part in living systems. Nevertheless, such progress was overshadowed by Pasteur's refutation of spontaneous generation which nearly extinguished experimental investigations into the origins of life for several decades.

Vitalism was dealt a deadly blow in the 1950's with Miller's famous spark-discharge experiments (Miller, 1953, 1955, 1957a, 1957b; Miller and Urey, 1959) which were undertaken in the framework of the Oparin (1924) and Haldane (1929) hypotheses concerning the origin of life. These hypotheses were constructed on some basic assumptions which included a reduced atmosphere, and a low surface temperature for the early Earth. These ideas meshed well with the prevailing hypothesis of the 1940's and 50's that the Earth had formed through heterogeneous accretion of dust from a condensing solar neb-

(NASA-CR-191257) HYDROTHERMAL
ORGANIC SYNTHESIS EXPERIMENTS
(Washington Univ.) 12 p

N73-13457

Unclass

G3/51 0131094

ula. Miller's experiments were extremely successful, and were followed by numerous other experiments by various investigators who employed a wide variety of energy sources for abiotic synthesis including spark discharges, ultra-violet radiation, heat, shock waves, plasmas, gamma rays, and other forms of energy. The conclusion reached from this body of work is that energy inputs can drive organic synthesis from a variety of inorganic starting materials.

1.1. ENVIRONMENTS FOR ORGANIC SYNTHESIS ON THE EARLY EARTH

A vast majority of the early abiotic synthesis experiments were based on an assumption that the primitive Earth had a reduced atmosphere consisting of gases such as CH_4 , NH_3 , H_2 , CO , and H_2O . This type of primary atmosphere was assumed to exist based on studies of the outer planets which are rich in reduced gases, together with the prevailing hypothesis of the midcentury that the Earth formed through relatively cool, heterogeneous accretion of material which condensed in a cooling solar nebula (Urey, 1952). Major difficulties with the heterogeneous accretion model are outlined by Ringwood (1979) and Stevenson (1983), and reviews of current models of the accretion of the Earth are given by Wetherill (1990), Taylor and Norman (1990) and Boss (1990). In these models, formation of planets through accretion is viewed as a violent process leading to considerable heating, melting and differentiation of planetary materials as planets form (Cameron, 1986; Benz *et al.*, 1987; Stevenson, 1987; Davies, 1990; Ringwood, 1990).

High velocity impacts of planetesimals onto a growing planet can result in the impact-degassing of volatiles and the formation of an impact-induced atmosphere at high temperature (Fegley *et al.*, 1986; Matsui and Abe, 1986a, 1986b; Holloway, 1988; Kasting, 1990). According to this hypothesis, the resulting impact-induced atmosphere contains carbon monoxide and/or carbon dioxide as the major forms of carbon. In addition, results of photochemical studies of the early Earth's atmosphere show that the presence of hydroxyl radicals from the photodissociation of H_2O , together with the greater flux of UV radiation from the young sun, would have limited the half lives of reduced gases such as methane and ammonia to about 50 years and about 1 week, respectively (Levine, 1982, 1985; Zahnle and Walker, 1982; Canuto *et al.*, 1982, 1983; Kasting *et al.*, 1983). Therefore, for a variety of reasons, the primitive Earth atmosphere may have been only "mildly reduced", which means it may have been similar to the present atmosphere but without high levels of O_2 . Some investigators view this as a problem for conventional chemical evolution theories because only a trace of amino acids is obtained in simulated primitive atmosphere experiments when carbon monoxide or carbon dioxide are used as carbon sources (Schlesinger and Miller, 1983).

On the other hand, if carbon in the early atmosphere was present as CO or CO_2 , organic molecules required for the origin of life could be formed in local "reducing" environments. Suggestions for such environments include impact sites of comets and/or meteorites, and submarine hydrothermal systems. The production of organic compounds in

the cooling gas mixtures formed during impacts has received recent attention (Chyba *et al.*, 1990; Chyba and Sagan, 1992). The oxidation states prevailing during large impacts will be strong functions of the composition of the target, which in the case of the Earth would likely lead to oxidized conditions (Fegley *et al.*, 1986). In contrast, submarine hydrothermal systems may provide the type of reduced environment needed for the abiotic synthesis of various organic compounds. In the present-day oceans, hydrothermal vents are more reduced than their immediate vicinity, and hydrothermal fluids are known to contain reduced gases such as methane, hydrogen, hydrogen sulfide, and ammonia (Lilley *et al.* 1983).

These observations have led several investigators to propose that abiotic organic synthesis can take place in hydrothermal systems (French, 1964, 1971; Ingmanson and Dowler, 1977; Corliss *et al.*, 1981; Baross and Hoffman, 1985; Shock, 1990b, 1992b). These suggestions are strengthened by the wide use of thermal energy for prebiotic synthesis experiments, and it is the purpose of this paper to summarize these experimental results, especially those involving aqueous solutions. However, as emphasized elsewhere (Shock, 1990b, 1992b), there is a great deal more to submarine hydrothermal systems than hot water. Oxidation states, gas fugacities, pH, and activities of aqueous ions are commonly buffered by mineral assemblages and fluid/rock reactions. Differences between the buffered conditions in natural systems and those which may be generated in unbuffered experiments can exceed many orders of magnitude. As a consequence, experiments solely involving heat as a source of energy are not likely to simulate realistic hydrothermal conditions even when an aqueous medium is used. This point is emphasized by reports in the literature of experiments conducted at the same temperature and pressure in which thermal energy has been used to drive aqueous organic synthesis reactions as well as reactions in which aqueous organic compounds are destroyed (Miller and Bada, 1988; Yanagawa *et al.*, 1988). The extent to which heat facilitates the synthesis or destruction of certain organic compounds at realistic hydrothermal conditions is not yet known. However, the body of relevant experimental work summarized below shows that there is great potential for organic synthesis in hydrothermal systems. One conclusion of this review is that this research area should be a prime target of further, well-constrained experiments.

2. Heat as an Energy Source for the Abiotic Synthesis of Organic Compounds

Heat is useful in two major ways in organic synthesis experiments. Reaction rates are enhanced by elevated temperatures, so reactions which may take millennia at room temperature are conducted at higher temperatures in order to conform to human lifespans. This application of thermal energy is often made in prebiotic experiments, and rates obtained at high temperatures are often extrapolated to lower temperatures by application of the Arrhenius equation (Abelson, 1957; Vallentyne, 1964; White, 1984; Miller and Bada,

1988). Additionally, the thermodynamic properties of reactions involving organic compounds are typically strongly temperature dependent, and increased temperatures may favor one set of reaction products over another. Often these two applications of thermal energy are employed simultaneously, as in the use of heat to drive polymerization reactions through dehydration (Schwartz *et al.*, 1975; Schwartz and Chittenden, 1976; Ivanov and Slavcheva, 1977; Epps *et al.*, 1978; Lahav *et al.*, 1978; Lawless and Levi, 1979; Lahav and White, 1980; Hawker and Oró, 1981a,b; Rishpon *et al.*, 1982; Rao *et al.*, 1982; Weber, 1989; among others, see below). Dehydration reactions also proceed in aqueous solution, and it has been shown that those which lead to peptide bonds are energetically more favorable at elevated temperatures than they are at 25°C and 1 bar (Flegmann and Tattersall, 1979; Shock, 1992a). In addition, theoretical calculations show that metastable equilibrium states in which aqueous organic compounds predominate are likely to be attainable at the elevated temperatures and pressures of submarine hydrothermal systems (Shock, 1990b, 1992b). Applications of thermal energy to synthesize organic compounds from inorganic starting materials and to polymerize organic compounds are reviewed in this section. Experiments related specifically to hydrothermal synthesis of organic compounds are described below.

2.1. THERMAL ORGANIC SYNTHESIS FROM INORGANIC COMPOUNDS

Several investigators have shown that thermal energy can be used to synthesize amino acids and other organic compounds from inorganic compounds in prebiotic experiments. For example, Harada and Fox (1964) synthesized amino acids from a mixture of CH₄, NH₃ and H₂O which had been passed through silica sand at 950°C, or through silica gel at 950° and 1050°C. After passing the gases through the hot silica, the products were collected in 3 N aqueous ammonia solutions which were then heated to 75°C for 35 hours. These authors reported the production of fourteen amino acids with glycine and alanine being the most abundant in all cases. Oró (1965) reported that at least a dozen amino acids were produced by reacting CH₄, NH₃ and H₂O at about 1025°C in a "hot tube" of unspecified composition. Glycine and alanine predominated by at least an order of magnitude in concentration over the other amino acids which included β-alanine, threonine, serine, and glutamic acid.

Silica gel was used by Taube *et al.* (1967) who heated a mixture of CH₄, NH₃ and H₂O (at a 5:3:2 ratio) in a streaming apparatus. As in the case of the experiments reported by Oró (1965), the residence time of the gas mixture in the reaction zone was very short (0.125 sec). Taube *et al.* (1967) found that the maximum conversion of NH₃ occurred at 1000°C (95.4%). Glutamic acid, lysine, proline, glycine, β-alanine, alanine, serine, valine, leucine, aminobutyric acid, and phenylalanine were identified, together with nitriles, amines, alcohols, aldehydes, aromatic hydrocarbons, CO, HCN and alkanes. Their yields of amino acids were lower at 900°C, and at 1150°C they observed that methane was converted to graphite. A similar experimental procedure was adopted by

Lawless and Boynton (1973) who used quartz sand and found only glycine and alanine in the samples run at 930°C; glycine, β -alanine, alanine and *N*-methyl- β -alanine at 980°C; and a variety of amino acids at 1060°C among which β -alanine was the most abundant by nearly two orders of magnitude.

These experiments are substantially similar to spark discharge experiments in that the spark temperatures are in the vicinity of 900°C (Fox and Dose, 1977). In both cases, enormous amounts of energy are used to generate high-energy radicals and other species which react on condensation in aqueous solution to yield amino acids and other organic compounds. Only in the vicinity of the magma/hydrothermal fluid interface are conditions in hydrothermal systems likely to be as severe than those imposed in traditional spark discharge or thermal synthesis experiments.

2.2. THERMAL ORGANIC SYNTHESIS FROM OTHER ORGANIC COMPOUNDS

Samochocka *et al.* (1968) synthesized amino acids by heating mixtures of acetylene and NH_3 (1:1 mol ratio) and acetylene, NH_3 and CO_2 (1:1:1 mol ratios) in quartz tubes heated to 600°C. The reacted gas mixtures were collected in H_2O and the resulting solutions were heated at 70°C for 35 hrs, and then evaporated. The residue was dissolved in 5N HCl and heated to 70°C for 5 hrs before analysis. Amino acids were produced from both initial gas mixtures, although a wider variety were found with CO_2 present. However, the CO_2 used was ^{14}C -labeled, and none of the amino or carboxylic acids produced contained radioactive carbon. The lack of radioactive labeling of products indicates that carbon from CO_2 was not incorporated in the products, and the authors state that this demonstrates that a Strecker synthesis did not occur in these experiments.

Other investigators, working at lower temperatures, have synthesized amino acids and other organic compounds from mixtures which include inorganic and simple organic compounds. For example, Oró *et al.* (1959) heated sealed glass vials containing aqueous mixtures of formaldehyde and hydroxylamine to 80°, 90° and 100°C for up to 400 hours. Ammonia was a major product but amino acids, HCN, carboxylic acids, and amides were also produced. The appearance and disappearance of the amides during the course of the experiments suggests that they were reaction intermediates to the formation of amino acids. Among the amino acids, glycine, alanine, and β -alanine were identified and aspartic acid, serine and threonine were tentatively identified. Formic, acetic, glycolic, and lactic acids were also produced in the experiments. Oró and Kamat (1961) report the formation of amino acids by heating solutions of HCN in 3 N ammonium hydroxide to 70°C for 25 days. Most of the HCN was converted to polymers, but the concentration of amino acids in the solution reached 10 mM (as glycine). Glycine, alanine and aspartic acid were tentatively identified by paper chromatography.

Aqueous formaldehyde and hydroxylamine were heated to 100°C for 150 hours in a solution of potassium phosphate and various trace elements by Ventilla and Egami (1977), who found that amino acids and oligomers of amino acids were formed although

no specific amino acids were identified. The same reactants were heated to 105°C in an aqueous solution of KCl and many trace constituents including Na^+ , Ca^{+2} , Mg^{+2} , SO_4^{-2} , HPO_4^{-2} , NO_3^- , Zn^{+2} , Fe^{+3} , Cu^{+2} , Co^{+2} , Mn^{+2} , and MoO_4^{-2} by Hatanaka and Egami (1977a, 1977b) who report the formation of many amino acids, and by Kamaluddin *et al.* (1979) who report the production of glycine, serine, aspartic acid and β -alanine, as well as NH_3 , urea, glycinenitrile and glycineamide. Amino acids were also produced by Yanagawa and Egami (1981) who heated similar aqueous solutions containing carbon suboxide (C_2O_3) polymers and hydroxylamine or ammonia to 105°C, and from solutions of sugars and ammonia (Yanagawa *et al.*, 1980, 1981), or oxo-acids and ammonia (Yanagawa *et al.*, 1982).

Mixtures of formaldehyde, ammonia and water were heated to 185°C by Fox and Windsor (1970) who report the formation of several amino acids, with glycine again being the predominant amino acid identified. Yields of amino acids were in the range 0.002 to 0.007 percent of the initial formaldehyde, and a major product of these reactions was hexamethylenetetramine. A wider spectrum of products was obtained by Lowe *et al.* (1963) who heated concentrated aqueous solutions of hydrocyanic acid, ammonia and oxalic acid to 90°C for 18 hours. More than ten amino acids were identified and evidence of several others was also found. In addition, ammonia, urea, adenine and formic acid were identified. In other aqueous thermal synthesis experiments, uracil was formed by heating solutions of urea, malic acid and polyphosphoric acid to 100°-140°C for up to 2 hrs (Fox and Harada, 1961), and aspartic acid and alanine were synthesized by heating ammonium malate and ammonium fumarate solutions to 200°C (Fox *et al.*, 1955).

More recent results from Kimoto and Fujinaga (1988, 1990) indicate that elevated temperatures may not be necessary for aqueous organic synthesis given the right initial mixture of compounds. These investigators obtained glycine, serine, and alanine, as well as poorly-defined polymers, at room temperature by mixing H_2S or Na_2S into aqueous solutions of ammonium formate, formaldehyde and magnesium chloride. These results may indicate that organic synthesis is possible in aqueous solution at the low temperatures which characterize seafloor weathering, but the concentrations of the reactants (5M HCOONH_4 , 0.1M formaldehyde) may greatly exceed the concentrations attainable in natural systems.

None of the experiments described above were designed to evaluate hydrothermal organic synthesis. In fact, most of this work predates the discovery of hot springs on the ocean floor. Although many of these experiments were conducted in aqueous solution, and it might seem attractive to assert that these experiments represent hydrothermal syntheses, many of the features which characterize hydrothermal systems are absent from these experiments. In particular, the buffered fugacities of H_2 , CO_2 , and activities of aqueous ions which characterize hydrothermal systems are not constrained or approached in these experiments. In addition, the experiments which employ simple organic compounds as starting materials are difficult to mesh with geologic systems unless a source of such starting materials can be established. Nevertheless, these results are tantalizing

glimmers of possible hydrothermal synthesis which can only be confirmed once properly constrained experiments have been conducted.

2.3. THERMAL POLYMERIZATION

It has been shown repeatedly that amino acids will polymerize under the influence of heat at elevated temperatures. Many of these experiments have been conducted at anhydrous conditions which strongly favor the dehydration reactions leading to peptide bond formation (Meggy, 1953, 1956; Kovacs *et al.*, 1953; Kovacs and Konyers, 1954; Heyns and Pavel, 1957a, 1957b; Fox *et al.*, 1957, 1959, 1963; Fox and Harada, 1958, 1960; Harada and Fox, 1958, 1960, 1965, 1975; Vegotsky *et al.*, 1958; Fox, 1963, 1964, 1965; Rohlfing, 1967, 1976; Fox and Waehneltdt, 1968; Saunders and Rohlfing, 1972, 1974; Phillips and Melius, 1974; Snyder and Fox, 1975; Rohlfing and McAlhaney, 1976; Fouche and Rohlfing, 1976; Temussi *et al.*, 1976; Fox and Dose, 1977; Grote *et al.*, 1978; Kokufuta *et al.*, 1978; Lacey *et al.*, 1979; Harada and Matsuyama, 1979; Hartmann *et al.*, 1981; Fox and Nakashima, 1981; among others). None of these results can be applied directly to hydrothermal systems because of the anhydrous nature of the experiments.

Other investigators have demonstrated polymerization of amino acids at elevated temperatures in aqueous solution. For example, Oró and Guidry (1961) polymerized glycine in aqueous solution at temperatures from 130° to 160°C. Lowe *et al.* (1963) formed polymers of amino acids at 90°C in some of the same aqueous solutions in which they synthesized amino acids. Nagayama *et al.* (1990) have shown that linear glycine peptides can be formed from diketopiperazines in aqueous solutions at 90°C. Rode and Schwendinger (1990) report that glycine will polymerize in 5M NaCl solutions containing Cu^{+2} at 70° to 100°C. The latter experiments demonstrated that the polymerization of glycine was enhanced by increasing the concentration of NaCl, decreasing the pH, and allowing the experiments to run for greater lengths of time. Using aqueous salt solutions including many transition metals, Yanagawa *et al.* (1980, 1988) and Yanagawa and Egami (1980) synthesized polymers of amino acids in solution at 105°C. Yanagawa and Kojima (1985), Yanagawa *et al.* (1988), and Yanagawa and Kobayashi (1992) were successful in synthesizing peptide-like polymers in aqueous solutions at temperatures $\geq 250^\circ\text{C}$ and elevated pressures.

3. Hydrothermal Destruction and Synthesis of Organic Compounds

Hydrothermal systems have been studied for many decades because they are responsible for a majority of the economically mined ore deposits of precious and base metals. In conjunction with field and analytical studies of ore deposits, hundreds of hydrothermal experiments involving minerals have been conducted by petrologists and geochemists. In these experimental efforts it has become crucial, and customary, to obtain reversals of various reactions in order to demonstrate equilibrium. Experiments are commonly con-

ducted with mineral/fluid systems which buffer pH, and/or the oxidation state of the experiment to values obtained from theoretical studies of mineral alteration and ore deposition, as well as analytical studies of present-day hot spring and geothermal systems. Careful attention to detail requires thorough analysis of reactants and products before and after these experiments are conducted. Results can then be interpreted with the aid of thermodynamic and kinetic calculations of speciation, solubility and mass transfer. References to hydrothermal experimental techniques and interpretation of the results can be found in Barnes (1979), Ulmer and Barnes (1987), Holloway and Wood (1988) and Spencer and Chou (1990).

In contrast, the rigor which characterizes the experimental study of hydrothermal minerals is distinctly lacking from most experimental studies of hydrothermal organic compounds. None of the work to date has attempted an experimental reversal of a reaction, and few if any constraints from studies of hydrothermal systems are imposed on these experiments. Typically, the lack of experimental constraint makes it impossible to link experimental conditions with those which exist in nature. Therefore, it comes as little surprise that there are reports in the literature of destruction and production of aqueous amino acids at the same temperatures and pressures. Descriptive variables other than temperature control the results of these experiments. Likely candidates include the fugacities of H_2 , CO_2 , and other gases, and the activities of aqueous species. The experiments leading to the destruction of amino acids, which represent one direction of reaction progress, are summarized in the next section, and those representing the opposite direction of reaction progress, amino acid production, are described below. It may be that well-constrained experiments will be undertaken in the near future, as many investigators appear to be realizing that their recent experiments do not come close to representing natural conditions or processes.

3.1. HYDROTHERMAL DESTRUCTION EXPERIMENTS

Many investigators have conducted experiments in which amino acids are altered into other organic or inorganic compounds at elevated temperatures (Abelson, 1957; Jones and Vallyntyne, 1960; Vallyntyne, 1964, 1968; Povoledo and Vallyntyne, 1964; White, 1984; Bernhardt *et al.*, 1984; Lavrent'yev *et al.*, 1985; Miller and Bada, 1988; Bada *et al.*, 1991), but none of the conditions imposed in these experiments can be considered to be close analogues of hydrothermal systems (Shock, 1990a, 1990b). The typical experimental procedure consists of preparing an aqueous solution of amino acids, enclosing the solution in a vessel, and heating the vessel--usually under pressure--to temperatures of 200°C or higher. No efforts are made to buffer fugacities of H_2 , CO_2 , NH_3 , N_2 , or any other component of the system. Occasionally efforts are made to buffer pH. However, this has been done with organic buffers, about which the temperature dependence of pKa is often unknown. Therefore, it is unclear to what extent the pH at elevated temperatures resembles those evaluated for hydrothermal systems. In addition, the buffers apparently

fail as demonstrated by experiments conducted by Miller and Bada (1988) who used HEPES (N2-hydroxyethylpiperazine N-2 ethane sulphonic acid) to buffer the 25°C pH to 7.0. After the experiment the pH was reported to be 7.9.

Reaction progress in these experiments is typically monitored by the disappearance of the amino acid(s) of interest. Only rarely are reaction products searched for and identified and none of the investigations referred to above made any effort to demonstrate mass balance. It is often established that heating solutions of amino acids causes the amino acid concentrations to decrease. These decreases are due to unknown reactions which may include decarboxylation, deamination, oxidation, reduction, polymerization or other processes. Lack of knowledge of the reactions involved has not inhibited several investigators from extracting rate data from these experiments and using such data to make inferences about the geochemistry of amino acids (Abelson, 1957; White, 1984; Miller and Bada, 1988). It is not apparent how useful a rate for an unknown, and possibly unnatural, reaction can be in understanding hydrothermal organic geochemistry. It should be noted that similar mysteries shroud the vast majority of hydrous pyrolysis experiments conducted in an effort to understand the generation of petroleum from organic-rich source rocks.

3.2. HYDROTHERMAL SYNTHESIS EXPERIMENTS

In contrast to the thermal synthesis and polymerization experiments discussed above, several researchers have synthesized organic compounds abiotically, and/or polymerized monomers at conditions much more reminiscent of hydrothermal systems. Probably the first study to document hydrothermal abiotic synthesis was strictly serendipitous. During his Ph.D. thesis research on the synthesis of siderite (FeCO_3) at metamorphic and hydrothermal conditions, French (1964) noted distinctive odors on opening reaction vessels. Gas chromatography indicated the presence of numerous organic compounds including ethanol; acetic, propanoic, and butanoic acids; and ketones. The purpose of the investigation was to synthesize siderite at hydrothermal conditions, and not organic compounds. As a consequence, these results receive only a brief mention in a later paper (French, 1971). Nevertheless, it would appear that the first proposal of organic synthesis in hydrothermal systems in the context of the origin of life was made by French who wrote: "The syntheses described here, which occur at elevated temperatures and pressures, may indicate that organic compounds could be produced by hydrothermal activity at shallow depths within the crust. If this were the case, the presence of such compounds on the surface would not reflect the composition of the atmosphere into which they were introduced." (French, 1964, p. 68). French (1971) expanded on this point and suggested that organic compounds synthesized in hydrothermal systems could reach the surface and provide "material for biological development even in cases where such synthetic reactions were not possible in the planetary atmosphere or oceans themselves." The perspective of

this statement is extraterrestrial, but at present it has terrestrial implications in light of the mounting evidence that a reduced atmosphere was unlikely on the early Earth.

In an effort to simulate the action of an "under water volcano," Mukhin (1976) exposed mixtures of H_2O (90%), NH_3 (5%) and CH_4 or CO (5%) to 1100-1200°C for ~0.1 sec in "quartz tubes with volcanic lava." Analysis of these solutions detected aldehydes and amino acids as well as many aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAH). Synthesis of PAH from CH_4 , and mixtures of CH_4 , NH_3 and H_2O at 1000°C is also reported by Oró and Han (1966). The appearance of PAH in these experiments bears a striking similarity to submarine hydrothermal systems on sedimented ridge systems (Kawka and Simoneit, 1990; Simoneit, 1990; Kvenvolden and Simoneit, 1990), although it is generally believed that PAH in hydrothermal systems are not synthesized from methane, but represent pyrolysis products of detrital organic matter. The total concentration of the amino acids in Mukhin's experiments was estimated to be 10^{-4} g l^{-1} . Mukhin (1976) suggests that amino acids formed through the hydrolysis of nitriles generated in the reaction zone. He supports this suggestion with the observation that the concentration of HCN in the solutions is nearly 10^{-2} g l^{-1} , and indicates that a Strecker mechanism may be involved in amino acid production.

Synthesis of amino acids at elevated temperatures (200-300°C) is apparently also possible by reacting ammonium carbonate solutions with carbides. This process is related to those involving carbides suggested by Oparin (1924), but which have never been adequately studied owing to arguments against the presence of carbides in the geologic record and the early success of spark-discharge and other synthesis methods. Marshall (1987) synthesized amines and hydrocarbons using Fe_3C as a reactant, and found that amino acids could be generated from CaC_2 at more oxidized conditions obtained by the addition of H_2O_2 (Marshall, 1992). Several amino acids were produced with this method, among which glycine, alanine and lysine typically predominated over aspartic acid, isoleucine, phenylalanine and other products (Marshall, 1992). Carbides are found in some meteorites, and it may be that these minerals are exposed to hydrothermal alteration. It is doubtful whether such reactions occur in present-day, terrestrial hydrothermal systems, but these results may have some bearing on organic synthesis on meteorite parent bodies. To the extent that processes which occurred on the early Earth can be understood from the study of meteorites, these experiments may be applicable to the study of the origin of life.

Recently, several investigators have begun efforts to synthesize amino acids and other organic compounds at conditions more representative of hydrothermal systems. Some of these results are reviewed here, and a summary of recent results by Yanagawa and Kobayashi is given in another paper in this volume. Preliminary results obtained by Hennessey *et al.* (1992) indicate that several amino acids including glycine, alanine, aspartic acid and isoleucine can be produced in aqueous solution at 150°C through a Strecker-like synthesis involving formaldehyde and HCN. The main feature which distinguishes these results from other hydrothermal synthesis experiments is that an attempt was made to

buffer the oxidation state with pyrite, pyrrhotite and magnetite, a mineral assemblage common to hydrothermal systems. Equilibration of an aqueous fluid with this buffer assemblage is likely to be sluggish at 150°C (Barnes, 1987), but experiments at higher temperatures may circumvent this kinetic barrier.

Despite the focus on amino acids in the preceding discussion, which stems from the emphasis placed on searching for these compounds in abiotic synthesis experiments, hydrothermal synthesis is not limited to amino acids. This was demonstrated recently in a study by Yamagata *et al.* (1991) who showed that polyphosphates can be generated by the action of H₂O vapor on a basaltic magma spiked with calcium phosphate. The same authors have found evidence of polyphosphate in volcanic gases exiting fumaroles at temperatures of 540-690°C.

4. Concluding Remarks

Thermal energy has a long and distinguished history in organic synthesis experiments, extending back at least to the early 1800's. The frenzy of experimental work which followed Miller's spark discharge experiments showed that heat could be used as an energy source in abiotic synthesis, and many of those experiments were done in aqueous solution. The success of these experiments is the basis of the many suggestions and scenarios in the literature for organic synthesis in hydrothermal systems (French, 1964, 1971; Ingmanson and Dowler, 1977; Corliss *et al.*, 1981; Baross and Hoffman, 1985; Shock, 1990b, 1992b). There is ample heat in submarine hydrothermal systems for driving abiotic synthesis reactions. Macdonald *et al.* (1980) calculated that the heat flow from a single black-smoker chimney was equivalent to the total heat loss for a 3- to 6-km segment of spreading center out to 10 km on either side. Hot springs on the East Pacific Rise at 21°N operate at temperatures up to and above 350°C with flow rates from 1 to 5 m sec⁻¹. Therefore, if heat can overcome kinetic barriers to the formation of metastable states from reduced or oxidized starting materials, abiotic synthesis at hydrothermal conditions is a distinct possibility (Shock, 1990b, 1992b). However, carefully controlled experiments which replicate the descriptive variables of natural hydrothermal systems (temperature, pressure, oxidation state, pH, inorganic fluid composition, etc.) have not yet been conducted with the aim of testing the hypothesis of hydrothermal organic synthesis. There are tantalizing results, especially in the experiments conducted by French (1964, 1971), which are consistent with metastable synthesis of organic compounds as postulated by Shock (1990b, 1992b). Well-constrained experimental tests of these hypotheses should be the next step.

Acknowledgements

This review benefitted from discussions with Dale Ingmanson, Bevan French, Mike Russell, Hiroshi Yanagawa, Bill Marshall, Nils Holm and Remy Hennet. Thanks are due

to Carla Koretsky and Patty DuBois for technical assistance, and Dale Ingmanson for his review of the manuscript. This work was funded in part by NSF grant EAR-9018468 and NASA grant NAGW-2818.